Abstract in English

The thesis entitled “Photophysical effects in single nanoobjects” prepared in the Advanced Materials Engineering and Modelling Group at the Faculty of Chemistry of Wrocław University of Science and Technology (WUST) was written under the supervision of dr hab. inż. Katarzyna Matczyszyn, Associate Professor of WUST. The original language of this work is English.

In this work experimental and computational studies on various materials’ response to continuous or femtosecond pulsed electromagnetic radiation are collected. These materials are characterised by nanoscopic-level of ordering leading to or having potential of higher-level arrangements widely known as hierarchical nanostructures. High-order arrangement having its source in nanoscale organisation leads to distinct photophysical effects, as is shown throughout this dissertation. The document is divided into three larger sections.

The section of introduction to photophysics involved in the observed processes (Chapter 1), including linear and non-linear absorption induced luminescence, Brillouin scattering and plasmonics, with most important sources, both theoretical and experimental, given as references. Also, methods utilised in obtaining the results are briefly introduced.

The research section (Chapters 2-4) is divided into a short introductory part consisting of: current knowledge about materials involved, sample or model preparation, and detailed methods applied; the results and discussion part describing in detail the findings; the conclusion part summarising the most important outcomes; finally, supplementary data is included. Each part is provided with crucial literature sources as references. Two of the chapters contain a part of results already published in peer-reviewed journals (Chapters 2 and 4) and a manuscript for results described in Chapter 3 is in production.

Finally, the section containing general conclusions concerns the obtained results and conclusions that can be drawn from them. Here, the focus is on issues solved during the studies, the open questions, and the outlook for the future research.

The results described in Chapters 2 and 3 concern quinacridone microcrystals with hierarchical nanostructures and quinacridone thin film. The crystals in this study were quinacridone platelets, and needle- or dagger-shaped radially protruding nanocrystals in the form of sphere-like microstructures. Chapter 2 is dedicated to optical non-linear spectroscopy of quinacridone microcrystals and thin film utilising two-photon excited luminescence microscopy technique with femtosecond-pulsed infrared laser operating in low fluence regime typically used in such experiments. It was shown that all of the studied structures exhibit two-photon excited luminescence, and that second-harmonic generation is a feature of only the samples containing well-developed surface. Power law dependence of the luminescence intensity as well as connection between the luminescence emission bands and crystalline order are discussed. The power law results indicate that various mechanisms of excited state deactivation are present. As for correlation between the spectral response and the structure, it is extensively discussed. The discussion settles at strong connection between well-developed structures displaying both second-harmonic generation and intense emission from defect states amply available in such structures. Currently, all quinacridone polymorphs are assigned to space groups with inversion centre, and thus are not expected to show second-harmonic generation as being symmetry-forbidden. Yet the strongly polycrystalline structures exhibit it in a narrow spectral range within the laser wavelength range available during the measurement, hence a connection is proposed between SHG and interface-induced symmetry breaking.

Chapter 3 is dedicated to transient measurements of multi-photon absorption-induced strain waves in the substrate of quinacridone thin film and to extended analysis of the results. The technique used in these measurements is Time-Domain Brillouin Scattering which utilises femtosecond-pulsed laser in high-fluence regime to generate strain through absorption of pump beam in the film and to probe differential reflectivity caused by Brillouin scattering on strain propagating in the substrate. The outcome satisfied cubic power law indicating absorption of three photons. Additional experiments of white light supercontinuum transient absorption were conducted to probe absorptive properties of quinacridone film in its electronic ground, first, and second excited states. The result indicated that the mechanism responsible for cubic power law is a sequential process of two-photon absorption followed by absorption of the third photon by the excited state. From XRD measurements thermal expansion coefficients of quinacridone polymorphs were extracted and together with assumed principal heat capacity of pentacene, which as a molecule is similar to quinacridone, included in a model allowing for connecting the generated strain with multi-photon absorption coefficients. The values determined for two-photon and three-photon absorption coefficients were, respectively, 1.45×10-49 cm4 s (14.5 GM) and 6.44×10-79 cm6 s2, therefore not record-breaking ones, but of the order of magnitude that may be expected for fused-ring molecules of that size. The point of this evaluation was to prove the feasibility of obtaining quantitative nonlinear cross-section data based on *ultrafast picosecond* photoacoustic approach and that it might become an alternative or an addition to other multi-photon techniques of non-linear coefficients determination. The results presented in Chapter 3 reveal complex photophysics of quinacridone including two-photon absorption and excited-state absorption, likely occurring from dark one-photon state. All results described in this chapter are a result of cooperation with the Matter and Light Department in the Institute of Physics of University of Rennes 1 and with the Department of Chemistry of Massachusetts Institute of Technology.

Chapter 4 is concerned with simulation of gold bipyramid dimers arranged in various configurations of angles and distances indicated in literature and obtained from TEM microscopy. The study encompasses finite-element simulations of circular dichroism and comprehensive analysis of the studied systems’ response to optical excitation. The analysis of the results includes consideration of handedness introduced to the simulation by substrate presence, yet it was found to be on numerical noise level and excluded from further discussion. There are three main findings from these simulations: 1) There is opposition of sign in absorption versus scattering differential cross-section at various interparticle angles and positionings on surface leading to explicitness of all structures’ spectral response. Considering so varied results for absorption and scattering these simulations show that it might be possible to determine bipyramid dimers structures without need of correlation with subwavelength techniques. 2) Size effects in dichroism are observed as dichroism reversal of sign with smaller size of bipyramid; 3) Large extinction g-factor (-0.3) or differential cross-section normalised by average is calculated and places the result among top values of other known dichroic structures in visible range of light spectrum. Such large dichroism signal obtained for two-particle system is promising when higher-order structures are made with gold bipyramids as chirality is known to increase with the number of particles.